

Supporting Information to

Orientalional Mobility in Dendrimer Melts: Molecular Dynamics Simulations

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1. Justification of equilibration times

Typically equilibration trajectories should be longer than the maximal characteristic time of various autocorrelation function (ACF). The ACF for radius of gyration, R_g , and the P_I^r ACF (i.e. for overall dendrimer rotation) are shown in Fig. S1. The maximal characteristic times are shorter than 5 ns and, therefore, we can conclude that 20 ns, which is used to equilibrate systems, is enough.

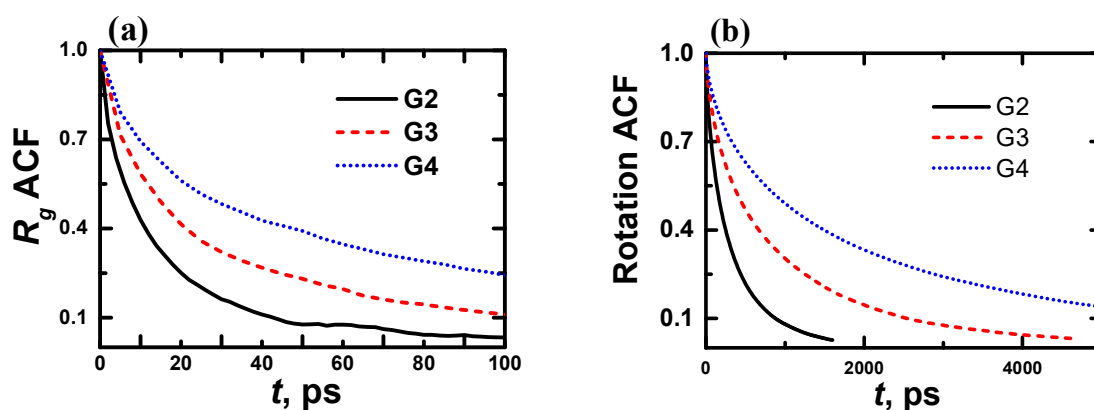


Figure S1. Autocorrelation functions for the radius of gyration (a) and overall rotation (b) for different generations of the PBC dendrimer.

2. Parameters of segments in different dendrimer layers.

The main parameters of viscoelastic modes, which are used in the analytical theory, are the effective friction of a branching point (bead) and the length of segments between beads. In framework of our MD simulations it is difficult to estimate the friction coefficient of beads. Therefore, in Fig. S2 we only show the distribution of the length of segments in different dendrimer shells.

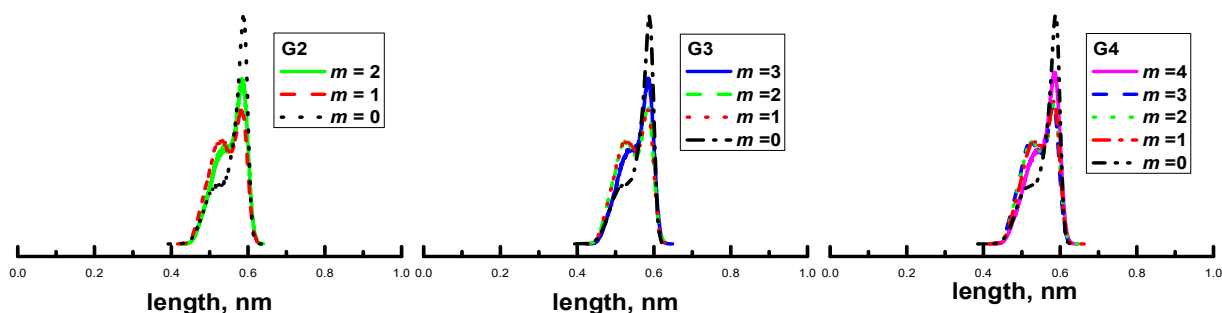


Figure S2. Distribution functions of the length of segments in different dendrimer layers for $G = 2, 3,$ and 4 . m is the layer number, which begins from the terminal layer.

3. The calculation of overall rotation times of dendrimer macromolecules

The characteristic time of rotation of a dendrimer macromolecule as a whole, τ_r , can be obtained from the $P_1^r(t, G)$ ACFs for the vector directed from the atom Si of a core to an atom Si of the terminal layer, i.e. for the unit vector $\mathbf{u} = \mathbf{r}_d / |\mathbf{r}_d|$ in Eq. (1). For these functions the averaging should be performed for all terminal Si atoms. The overall rotation time, τ_r , is calculated from the asymptotic slope of the $P_1^r(t, G)$ ACFs.

The calculated P_1^r ACFs for PBC dendrimers with $G = 2, 3$, and 4 generation at 600 K are shown in Fig. S3. The slope of the $\ln(P_1^r)$ function is determined by the inverse characteristic time of rotation of a dendrimer macromolecule as a whole. The results of the calculations are collected in Table S1.

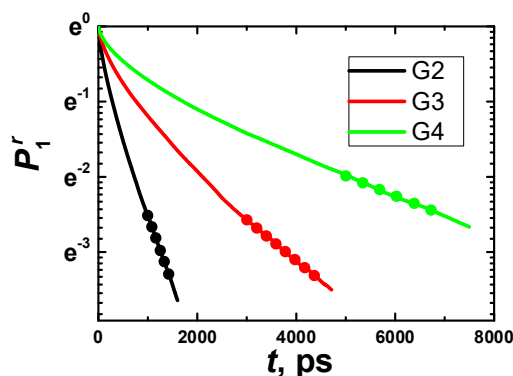


Figure S3. The time dependences of the P_1^r ACF for the PBC dendrimers with $G = 2, 3$, and 4 at 600 K (solid lines). The dots are the linear approximation of the $\ln(P_1^r)$ at long times.

4. The approximation of the P_1 ACFs.

For the approximation of the P_1 ACFs the Eq. (3) is used with the fixed τ_r . The results of approximation are presented in Tab. S1. The obtained fitting curves can be

seen in Fig. S4. For the additional illustration the times (τ_r , τ_m^{br} , τ_{in}) as functions of molecular weight are shown in Fig. S5.

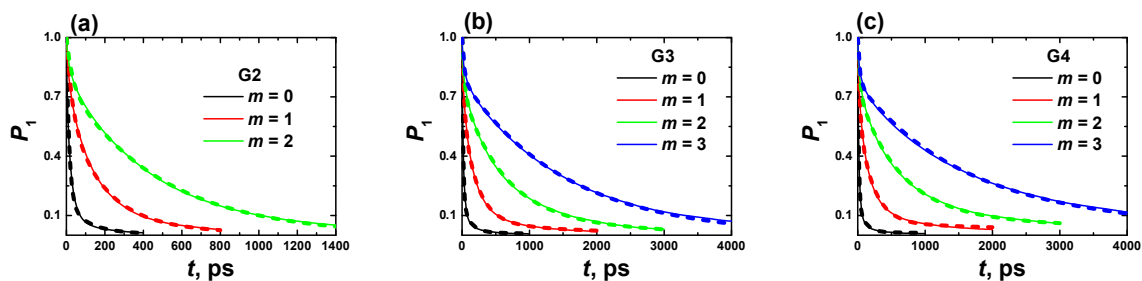


Figure S4. The time dependences of the P_1 ACF for the PBC dendrimers with $G = 2-4$ at 600 K (solid lines) and the fitting functions (dashed lines). m is the layer number, which begins from the terminal layer (see Fig. 1a).

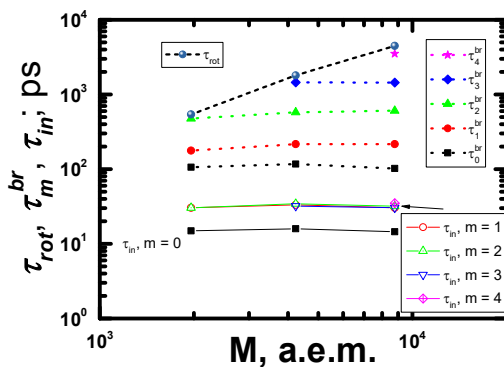


Figure S5. The characteristic times for P_1 ACFs vs molecular weight.

Table S1. The approximation of the P_1 ACF. τ_r^G is the rotation time of a dendrimer macromolecule as a whole; τ_{in} is the averaged time of the internal spectrum, corresponding to the small-scale mobility; τ_m^{br} is the pulsation time of the branch; C_{in} , C_{br} , and C_r are the relative contributions of the modes with corresponding times to the P_1 ACF; m is the layer number, which begins from the terminal layer (see Fig. 1a).

G	τ_r^G , ps	m	τ_{in} , ps	τ_m^{br} , ps	C_{in}	C_{br}	C_r
2	540	0	14.9	106	0.835	0.15	0.015
		1	30.4	177	0.36	0.555	0.085
		2	30.3	475	0.23	0.59	0.18
3	1800	0	15.9	117	0.835	0.15	0.015
		1	33.2	216	0.38	0.55	0.07
		2	34.3	578	0.27	0.59	0.14
		3	32	1450	0.21	0.6	0.19
4	4470	0	14.5	102	0.835	0.15	0.015
		1	30.3	216	0.387	0.55	0.063
		2	31.8	607	0.27	0.62	0.11
		3	30.4	1440	0.23	0.59	0.18
		4	35	3515	0.19	0.53	0.28

5. The frequency dependences of ^{13}C NMR relaxation rates

In addition to the data on proton relaxation (see the main text), we present the data on the ^{13}C relaxation which can be useful for future discussions.

In the assumed dipole-dipole approximation, the ^{13}C NMR relaxation rates can be expressed through spectral densities, $J(\omega)$, by following expressions:

$$[R_{1C}]_{\omega} = \frac{\omega_C}{A_{0C}} \left(\frac{1}{T_{1C}} \right) = \omega_C [6J(4.976\omega_C) + J(2.976\omega_C) + 3J(\omega_C)], \quad (\text{S1})$$

for the spin-lattice relaxation and

$$[R_{2C}]_{\omega} = \frac{2\omega_C}{A_{0C}} \left(\frac{1}{T_{2C}} \right) = \omega_C [4J(0) + J(2.976\omega_C) + 3J(\omega_C) + 6J(3.976\omega_C) + 6J(4.976\omega_C)], \quad (\text{S2})$$

for the spin-spin relaxation. Here ω_C is the cyclic frequency of the carbon nucleus; A_{0C} is the constant which does not depend on the frequency and temperature.

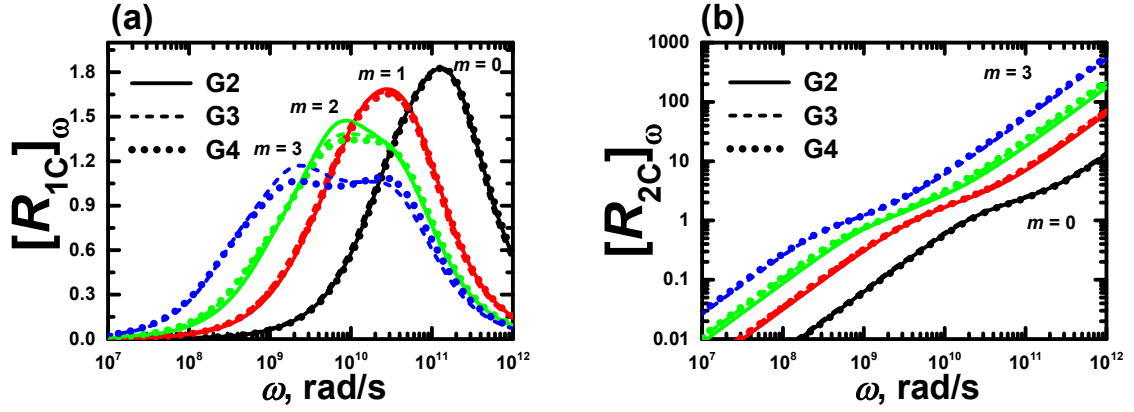


Figure S6. Frequency dependences of spin-lattice (a) and spin-spin (b) reduced relaxation rates for the individual segment in different layers. m is the layer number, which begins from the terminal layer.